

Thermodynamics and HYSYS

Workshop

One of the main assets of HYSYS is its strong thermodynamic foundation. Not only can you use a wide variety of internal property packages, you can use tabular capabilities to override specific property calculations for more accuracy over a narrow range. Or, you can use the functionality provided through OLE to interact with externally constructed property packages.

The built-in property packages in HYSYS provide accurate thermodynamic, physical and transport property predictions for hydrocarbon, non-hydrocarbon, petrochemical and chemical fluids. The database consists of an excess of 1500 components and over 16000 fitted binary coefficients. If a library component cannot be found within the database, a comprehensive selection of estimation methods is available for creating fully defined hypothetical components.

HYSYS also contains a regression package within the tabular feature. Experimental pure component data, which HYSYS provides for over 1000 components, can be used as input to the regression package. Alternatively, you can supplement the existing data or supply a set of your own data. The regression package will fit the input data to one of the numerous mathematical expressions available in HYSYS. This will allow you to obtain simulation results for specific thermophysical properties that closely match your experimental data.

However, there are cases when the parameters calculated by HYSYS are not accurate enough, or cases when the models used by HYSYS do not predict the correct behaviour of some liquid-liquid mixtures (azeotropic mixtures). For those cases it is recommended to use another of Hyprotech's products, DISTIL. This powerful simulation program provides an environment for exploration of thermodynamic model behaviour, proper determination and tuning of interaction parameters and physical properties, as well as alternative designs for distillation systems.

Proper use of thermodynamic property package parameters is key to successfully simulating any chemical process. Effects of pressure and temperature can drastically alter the accuracy of a simulation given missing parameters or parameters fitted for different conditions. HYSYS is user friendly by allowing quick viewing and changing of the particular parameters associated with any of the property packages. In addition, you are able to quickly check the results of one set of parameters and compare those results with another set.

In this module, you will explore the thermodynamic packages of HYSYS and the proper use of their thermodynamic parameters.

Learning Objectives

Once you have completed this module, you will be able to:

- Select an appropriate Property Package
- Understand the validity of each Activity Model
- Enter new interaction parameters for a property package
- Check multiphase behaviour of a stream
- Understand the importance of properly regressed binary coefficients

Selecting Property Packages

The property packages available in HYSYS allow you to predict properties of mixtures ranging from well defined light hydrocarbon systems to complex oil mixtures and highly non-ideal (non-electrolytic) chemical systems. HYSYS provides enhanced equations of state (**PR** and **PRSV**) for rigorous treatment of hydrocarbon systems; semi-empirical and vapour pressure models for the heavier hydrocarbon systems; steam correlations for accurate steam property predictions; and activity coefficient models for chemical systems. All of these equations have their own inherent limitations and you are encouraged to become more familiar with the application of each equation.

The following table lists some typical systems and recommended correlations:

Type of System	Recommended Property Package
TEG Dehydration	PR
Sour Water	PR, Sour PR
Cryogenic Gas Processing	PR, PRSV
Air Separation	PR, PRSV
Atm Crude Towers	PR, PR Options, GS
Vacuum Towers	PR, PR Options, GS <10mm Hg, Braun K10, Esso K
Ethylene Towers	Lee Kesler Plocker
High H ₂ Systems	PR, ZJ or GS (see T/P limits)
Reservoir Systems	PR, PR Options
Steam Systems	Steam Package, CS or GS
Hydrate Inhibition	PR
Chemical Systems	Activity Models, PRSV
HF Alkylation	PRSV, NRTL (Contact Hyprotech)
TEG Dehydration with Aromatics	PR (Contact Hyprotech)

Equations of State

For oil, gas and petrochemical applications, the Peng-Robinson EOS (PR) is generally the recommended property package. HYSYS currently offers the enhanced Peng-Robinson (PR) and Soave-Redlich-Kwong (SRK) equations of state. In addition, HYSYS offers several methods which are modifications of these property packages, including PRSV, Zudkevitch Joffe (ZJ) and Kabadi Danner (KD). Lee Kesler Plocker (LKP) is an adaptation of the Lee Kesler equations for mixtures, which itself was modified from the BWR equation. Of these, the Peng-Robinson equation of state supports the widest range of operating conditions and the greatest variety of systems. The Peng-Robinson and Soave-Redlich-Kwong equations of state (EOS) generate all required equilibrium and thermodynamic properties directly. Although the forms of these EOS methods are common with other commercial simulators, they have been significantly enhanced by Hyprotech to extend their range of applicability.

- The Peng-Robinson property package options are **PR**, **Sour PR**, and **PRSV**.
- Soave-Redlich-Kwong equation of state options are the **SRK**, **Sour SRK**, **KD** and **ZJ**.

For the Chemical industry due to the common occurrence of highly non-ideal systems, the PRSV EOS may be considered. It is a two-fold modification of the PR equation of state that extends the application of the original PR method for highly non-ideal systems.

- It has shown to match vapour pressure curves of pure components and mixtures, especially at low vapour pressures.
- It has been successfully extended to handle non-ideal systems giving results as good as those obtained by activity models.
- A limited amount of non-hydrocarbon interaction parameters are available.

Activity Models

Although equation of state models have proven to be very reliable in predicting properties of most hydrocarbon based fluids over a large range of operating conditions, their application has been limited to primarily non-polar or slightly polar components. Polar or non-ideal chemical systems have traditionally been handled using dual model approaches.

Activity Models are much more empirical in nature when compared to

the property predictions in the hydrocarbon industry. For example, they cannot be used as reliably as the equations of state for generalized application or extrapolating into untested operating conditions. Their tuning parameters should be fitted against a representative sample of experimental data and their application should be limited to moderate pressures.

For every component i in the mixture, the condition of thermodynamics equilibrium is given by the equality between the fugacities of the liquid phase and vapour phase. This feature gives the flexibility to use separate thermodynamic models for the liquid and gas phases, so the fugacities for each phase have different forms. In this approach:

- an equation of state is used for predicting the vapour fugacity coefficients (*normally ideal gas assumption or the Redlich Kwong, Peng-Robinson or SRK equations of state, although a Virial equation of state is available for specific applications*)
- an activity coefficient model is used for the liquid phase.

Although there is considerable research being conducted to extend equation of state applications into the chemical industry (e.g., PRSV equation), the state of the art of property predictions for chemical systems is still governed mainly by Activity Models.



Activity Models produce the best results when they are applied in the operating region for which the interaction parameters were regressed.

Activity coefficients are “fudge” factors applied to the ideal solution hypothesis (Raoult’s Law in its simplest form) to allow the development of models which actually represent real data. Although they are “fudge” factors, activity coefficients have an exact thermodynamic meaning as the ratio of the fugacity coefficient of a component in a mixture at P and T , and the fugacity coefficient of the pure component at the same P and T . *Consequently, more caution should be exercised when selecting these models for your simulation.*

The following table briefly summarizes recommended activity coefficient models for different applications (refer to the bulleted reference guide below):

Application	Margules	van Laar	Wilson	NRTL	UNIQUAC
Binary Systems	A	A	A	A	A
Multicomponent Systems	LA	LA	A	A	A
Azeotropic Systems	A	A	A	A	A
Liquid-Liquid Equilibria	A	A	N/A	A	A
Dilute Systems	?	?	A	A	A
Self-Associating Systems	?	?	A	A	A
Polymers	N/A	N/A	N/A	N/A	A
Extrapolation	?	?	G	G	G

- **A** = Applicable
- **N/A** = Not Applicable
- **?** = Questionable
- **G** = Good
- **LA** = Limited Application

Overview of Models

Margules

One of the earliest activity coefficient expressions was proposed by Margules at the end of the 19th century.

- The Margules equation was the first Gibbs excess energy representation developed.
- The equation does not have any theoretical basis, but is useful for quick estimates and data interpolation.
- In its simplest form, it has just one adjustable parameter and can represent mixtures which feature symmetric activity coefficient curves.



The Margules equation should not be used for extrapolation beyond the range over which the energy parameters have been fitted.

HYSYS has an extended multicomponent Margules equation with up to four adjustable parameters per binary. The four adjustable parameters for the Margules equation in HYSYS are the a_{ij} and a_{ji} (temperature independent) and the b_{ij} and b_{ji} terms (temperature dependent).

- The equation will use parameter values stored in HYSYS or any user supplied value for further fitting the equation to a given set of data.
- In HYSYS, the equation is empirically extended and therefore caution should be exercised when handling multicomponent mixtures.

van Laar



The van Laar equation performs poorly for dilute systems and CANNOT represent many common systems, such as alcohol-hydrocarbon mixtures, with acceptable accuracy.

The van Laar equation was the first Gibbs excess energy representation with physical significance. This equation fits many systems quite well, particularly for LLE component distributions. It can be used for systems that exhibit positive or negative deviations from Raoult's Law. Some of the advantages and disadvantage for this model are:

- Generally requires less CPU time than other activity models.
- It can represent limited miscibility as well as three phase equilibrium.
- It cannot predict maxima or minima in the activity coefficient and therefore, generally performs poorly for systems with halogenated hydrocarbons and alcohols.
- It also has a tendency to predict two liquid phases when they do not exist.

The van Laar equation implemented in HYSYS has two parameters with linear temperature dependency, thus making it a four parameter model. In HYSYS, the equation is empirically extended and therefore its use should be avoided when handling multicomponent mixtures.

Wilson

The Wilson equation, proposed by Grant M. Wilson in 1964, was the first activity coefficient equation that used the local composition model to derive the Gibbs Excess energy expression. It offers a thermodynamically consistent approach to predicting multi-component behaviour from regressed binary equilibrium data.



The Wilson equation CANNOT be used for problems involving liquid-liquid equilibrium.

- Although the Wilson equation is more complex and requires more CPU time than either the van Laar or Margules equations, it can represent almost all non-ideal liquid solutions satisfactorily except electrolytes and solutions exhibiting limited miscibility (LLE or VLLE).
- It performs an excellent job of predicting ternary equilibrium using parameters regressed from binary data only.
- It will give similar results to the Margules and van Laar equations for weak non-ideal systems, but consistently outperforms them for increasingly non-ideal systems.
- It cannot predict liquid-liquid phase splitting and therefore should only be used on problems where demixing is not an issue.

Our experience shows that the Wilson equation can be extrapolated with reasonable confidence to other operating regions with the same set of regressed energy parameters.



The additional parameter in the NRTL equation, called the alpha term, or non-randomness parameter, represents the inverse of the coordination number of molecule "i" surrounded by molecules "j". Since liquids usually have a coordination number between 3 and 6, you might expect the alpha parameter between 0.17 and 0.33.

NRTL

The NRTL (Non-Random-Two-Liquid) equation, proposed by Renon and Prausnitz in 1968, is an extension of the original Wilson equation. It uses statistical mechanics and the liquid cell theory to represent the liquid structure. These concepts, combined with Wilson's local composition model, produce an equation capable of representing VLE, LLE, and VLLE phase behaviour. Like the Wilson equation, the NRTL model is thermodynamically consistent and can be applied to ternary and higher order systems using parameters regressed from binary equilibrium data. The NRTL model has an accuracy comparable to the Wilson equation for VLE systems.

- The NRTL combines the advantages of the Wilson and van Laar equations.

- It is not extremely CPU intensive.
- It can represent LLE quite well.
- However, because of the mathematical structure of the NRTL equation, it can produce erroneous multiple miscibility gaps.

The NRTL equation in HYSYS contains five adjustable parameters (temperature dependent and independent) for fitting per binary pair.

UNIQUAC

The UNIQUAC (UNIversal QUAsi Chemical) equation proposed by Abrams and Prausnitz in 1975 uses statistical mechanics and the quasi-chemical theory of Guggenheim to represent the liquid structure. The equation is capable of representing LLE, VLE and VLLE with accuracy comparable to the NRTL equation, but without the need for a non-randomness factor, it is a two parameter model.

The UNIQUAC equation is significantly more detailed and sophisticated than any of the other activity models.

- Its main advantage is that a good representation of both VLE and LLE can be obtained for a large range of non-electrolyte mixtures using only two adjustable parameters per binary.
- The fitted parameters usually exhibit a smaller temperature dependence which makes them more valid for extrapolation purposes.
- The UNIQUAC equation utilizes the concept of local composition as proposed by Wilson. Since the primary concentration variable is a surface fraction as opposed to a mole fraction, it is applicable to systems containing molecules of very different sizes and shape, such as polymer solutions.
- The UNIQUAC equation can be applied to a wide range of mixtures containing H₂O, alcohols, nitriles, amines, esters, ketones, aldehydes, halogenated hydrocarbons and hydrocarbons.

In its simplest form it is a two parameter model, with the same remarks as Wilson and NRTL. UNIQUAC needs van der Waals area and volume parameters, and those can sometimes be difficult to find, especially for non-condensable gases (although DIPPR has a fair number available).

Extended and General NRTL

The Extended and General NRTL models are variations of the NRTL model, simple NRTL with a complex temperature dependency for the a_{ij} and a_{ji} terms. Apply either model to systems:



The general NRTL model is particularly susceptible to inaccuracies if the model is used outside of the intended range.

Care must be taken to ensure that you are operating within the bounds of the model.

- with a wide boiling point range between components
- where you require simultaneous solution of VLE and LLE, and there exists a wide boiling range or concentration range between components

Extreme caution must be exercised when extrapolating beyond the temperature and pressure ranges used in regression of parameters. Due to the larger number of parameters used in fitting, inaccurate results can be obtained outside the original bounds.

Chien-Null

Chien-Null is an empirical model designed to allow you to mix and match models which were created using different methods and combined into a multicomponent expression. The Chien-Null model provides a consistent framework for applying existing activity models on a binary by binary basis. In this manner, Chien-Null allows you to select the best activity model for each pair in the case. For example, Chien-Null can allow the user to have a binary defined using NRTL, another using Margules and another using van Laar, and combine them to perform a three component calculation, mixing three different thermodynamic models.

The Chien Null model allows 3 sets of coefficients for each component pair, accessible via the A, B and C coefficient matrices.

The Thermodynamics appendix in the HYSYS User Manual provides more information on Property Packages, Equations of State, and Activity Models, and the equations for each.



No interaction between "non-condensable" component pairs is taken into account in the VLE calculations.

Henry's Law

Henry's Law cannot be selected explicitly as a property method in HYSYS. However, HYSYS will use Henry's Law when an activity model is selected and "non-condensable" components are included within the component list.

HYSYS considers the following components non-condensable: Methane, Ethane, Ethylene, Acetylene, Hydrogen, Helium, Argon, Nitrogen, Oxygen, NO, H₂S, CO₂, and CO.

The extended Henry's Law equation in HYSYS is used to model dilute solute/solvent interactions. "Non-condensable" components are defined as those components that have critical temperatures below the system temperature.

Activity Model Vapour Phase Options

There are several methods available for calculating the Vapour Phase in conjunction with the selected liquid activity model. The choice will depend on specific considerations of your system.

Ideal

The ideal gas law can be used to model the vapour phase. This model is appropriate for low pressures and for a vapour phase with little intermolecular interaction. The model is the default vapour phase fugacity calculation method for activity coefficient models.

Peng Robinson, SRK or RK

To model non-idealities in the vapour phase, the **PR**, **SRK**, or **RK** options can be used in conjunction with an activity model.

- **PR** and **SRK** vapour phase models handle the same types of situations as the **PR** and **SRK** equations of state.
- When selecting one of these three models, ensure that the binary interaction parameters used for the activity model remain applicable with the chosen vapour model.
- For applications with compressors and turbines, **PR** or **SRK** will be superior to the **RK** or Ideal vapour model.

Virial



Care should be exercised in choosing PR, SRK, RV or Virial to ensure binary coefficients have been regressed with the corresponding vapour phase model.

The **Virial** option enables you to better model vapour phase fugacities of systems displaying strong vapour phase interactions. Typically this occurs in systems containing carboxylic acids, or compounds that have the tendency to form stable H_2 bonds in the vapour phase.

HYSYS contains temperature dependent coefficients for carboxylic acids. You can overwrite these by changing the Association (ij) or Solvation (ii) coefficients from the default values.

This option is restricted to systems where the density is moderate, typically less than one-half the critical density.

Binary Coefficients

For the Property Packages which do include binary coefficients, the **Binary Coefficients** tab contains a matrix which lists the interaction parameters for each component pair. Depending on the property method chosen, different estimation methods may be available and a different view may be shown. You have the option of overwriting any library value.

Equation of State Interaction Parameters

The **Equation of State Interaction Parameters** group appears as follows on the **Binary Coeffs** tab when an EOS is the selected property package:



The numbers appearing in the matrix are initially calculated by HYSYS, but you have the option of overwriting any library value.

Fluid Package: Stripper

Equation of State Interaction Parameters

	Chloroform	Toluene	H2O	Oxygen	Nitrogen
Chloroform	---	0.00000	0.00000	0.00000	0.00000
Toluene	0.00000	---	0.50000	0.00000	0.19320
H2O	0.00000	0.50000	---	0.00000	-0.31560
Oxygen	0.00000	0.00000	0.00000	---	-0.01200
Nitrogen	0.00000	0.19320	-0.31560	-0.01200	---

Treatment of Interaction Coefficients Unavailable from the Library:
☒ Estimate HC-HC / Set Non HC-HC to 0.0 ☐ Set All to 0.0

Prop Pkg / Components / Parameters / **Binary Coeffs** / StabTest / Rxns / Tabular / Notes

Delete Name: Stripper Property Pkg: Sour PR

For all EOS parameters (except PRSV),

$$K_{ij} = K_{ji}$$

so when you change the value of one of these, both cells of the pair automatically update with the same value. In many cases, the library interaction parameters for PRSV do have $K_{ij} = K_{ji}$, but HYSYS does not force this if you modify one parameter in a binary pair.

If you are using **PR** or **SRK** (or one of the Sour options), two radio buttons are displayed at the bottom of the page in the **Treatment of Interaction Coefficients Unavailable from the Library** group:

- **Estimate HC-HC/Set Non HC-HC to 0.0** – this radio button is the default selection. HYSYS provides the estimates for the interaction parameters in the matrix, setting all non-hydrocarbon pairs to 0.
- **Set All to 0.0** – when this is selected, HYSYS sets all interaction parameter values in the matrix to 0.0.

Activity Model Interaction Parameters

Activity Models are much more empirical in nature when compared to the property predictions in the hydrocarbon industry. Their tuning parameters should be fitted against a representative sample of experimental data and their application should be limited to moderate pressures.

The **Activity Model Interaction Parameters** group appears as follows on the **Binary Coeffs** tab when an **Activity Model** is the selected property package:

Fluid Package: Stripper

Activity Model Interaction Parameters

Coeff Matrix To View: ☒ Aij ☐ Bij ☐ Alpha_{ij} / C_{ij}

	Chloroform	Toluene	Ethanol	H2O	Oxygen	Nitrogen
Chloroform	---	-583.617	-285.388	4571.081	-12.163	---
Toluene	629.221	---	396.209	4293.937	-12.163	---
Ethanol	1289.218	1137.062	---	1332.312	-12.163	---
H2O	62226.371	5642.370	-109.634	---	-12.163	---
Oxygen	1522.574	1430.040	2414.426	1863.905	---	---
Nitrogen	-62.538	-197.751	1280.524	602.209	0.000	---

Coeff Estimation

☒ UNIFAC VLE
☐ UNIFAC LLE
☐ Immiscible

Individual Pair
 Unknowns Only
 ALL Binaries
 Reset Params.

R = 1.98721 cal/gmol K

Prop Pkg Components Parameters **Binary Coeffs** StabTest Rxns Tabular Notes

Delete Name Stripper Property Pkg NRTL

The interaction parameters for each binary pair will be displayed. You can overwrite any value or use one of the estimation methods.

Note that the $K_{ij} = K_{ji}$ rule does not apply to Activity Model interaction parameters.

Estimation Methods

When using Activity Models, HYSYS provides three interaction parameter estimation methods. Select the estimation method by choosing one of the radio buttons in the **Coeff Estimation** window. The options are:

- UNIFAC VLE
- UNIFAC LLE
- Immiscible

You can then invoke the estimation by selecting one of the available cells.

For UNIFAC methods the options are:

- **Individual Pair** – calculates the parameters for the selected component pair, A_{ij} and A_{ji} . The existing values in the matrix are overwritten.
- **Unknowns Only** – calculates the activity parameters for all the unknown pairs. If you delete the contents of cells or if HYSYS does not provide default values, you can use this option.
- **All Binaries** – recalculates all the binaries of the matrix. If you had changed some of the original HYSYS values, you could use this to have HYSYS re-estimate the entire matrix.

When the *All Binaries* button is used, HYSYS does not return the original library values. Estimation values will be returned using the selected UNIFAC method. To return to the original library values, you must select a new property method and then re-select the original property method



The UNIFAC (UNIquac group-Functional Activity Coefficient) method is a group contribution technique using the UNIQUAC model as the starting point to estimate binary coefficients. This, however, should be a last solution as it is preferable to try and find values estimated from experimental data.

For the Immiscible method the options are:

- **Row in Clm pair** – estimates the parameters such that the row component (j) is immiscible in the column component (i).
- **Clm in Row pair** – estimates parameters such that the column component (j) is immiscible in the row component (i).
- **All in Row** – estimates parameters such that both components are mutually immiscible.

In Module 1, you chose the NRTL Activity Model, then select the UNIFAC VLE estimation method (default) before pressing the **Unknowns Only** cell.

Which Activity Coefficient Model Should I Use?

This is a tough question to answer, but some guidelines are provided. If you require additional assistance, it is best to contact Hyprotech's Technical Support department.

Basic Data

Activity coefficient models are empirical by nature and the quality of their prediction depends on the quality and range of data used to determine the parameters. Some important things you should be aware of in HYSYS.

- The parameters built in HYSYS were fitted at 1 atm wherever possible, or were fitted using isothermal data which would produce pressures closest to 1 atm. They are good for a first design, but always look for experimental data closer to the region you are working in to confirm your results.
- The values in the HYSYS component database are defined for VLE only, hence the LLE prediction may not be very good and additional fitting is necessary.
- Data used in the determination of built in interaction parameters very rarely goes below 0.01 mole fraction, and extrapolating into the ppm or ppb region can be risky.
- Again, because the interaction parameters were calculated at modest pressures, usually 1 atm, they may be inadequate for processes at high pressures.
- Check the accuracy of the model for azeotropic systems. Additional fitting may be required to match the azeotrope with acceptable accuracy. Check not only for the temperature, but for the composition as well.
- If three phase behaviour is suspected, additional fitting of the parameters may be required to reliably reproduce the VLLE equilibrium conditions.

UNIFAC or no UNIFAC?

UNIFAC is a handy tool to give initial estimates for activity coefficient models. Nevertheless keep in mind the following:

- Group contribution methods are always approximate and they are not substitutions for experimental data.
- UNIFAC was designed using relatively low molecular weight condensable components (thus high boilers may not be well represented), using temperatures between 0-150 °C and data at modest pressures.

- Generally, UNIFAC does not provide good predictions for the dilute region.

Choosing an Activity Model

Again, some general guidelines to consider.

- **Margules** or **van Laar** - generally chosen if computation speed is a consideration. With the computers we have today, this is usually not an issue. May also be chosen if some preliminary work has been done using one of these models.
- **Wilson** - generally chosen if the system does not exhibit phase splitting.
- **NRTL** or **UNIQUAC** - generally chosen if the system exhibits phase splitting.
- **General NRTL** - should only be used if an abundant amount of data over a wide temperature range was used to define its parameters. Otherwise it will provide the same modelling power as NRTL.

Exploring with the Simulation

Proper use of thermodynamic property package parameters is key to successfully simulating any chemical process. Effects of pressure and temperature can drastically alter the accuracy of a simulation given missing parameters or parameters fitted for different conditions. HYSYS is user friendly in allowing quick viewing and changing of the particular parameters associated with any of the property packages. Additionally, the user is able to quickly check the results of one set of parameters and compare against another.

Exercise 1

Di-iso-Propyl-Ether/H₂O Binary

This example effectively demonstrates the need for having interaction parameters. Do the following:

1. Open case **DIPE.hsc**.
2. Enter the following conditions for stream **DIPE/H₂O**:

Conditions	
Vapour Fraction	0.0
Pressure	1 atm
Molar Flow	1 kgmole/h (1 lbmole/hr)
Composition	
di-i-P-Ether	50 mole %
H ₂ O	50 mole %



What phases are present? _____

3. Close the stream view and press the **Enter Basis Environment** button.
4. Select the **Binary Coeffs** tab of the Fluid Package. Notice that the interaction parameters for the binary are both set to 0.0.
5. Press the **Reset Params** button to recall the default NRTL activity coefficient model interaction parameters.
6. Close the Fluid Package view.
7. Return to the simulation environment by pressing the **Return to Simulation Environment** button.
8. Open the stream view by double clicking on the stream **DIPE/H₂O**.



What phases are now present? _____

What is the composition of each? _____

Clearly, it can be seen how important it is to have interaction parameters for the thermodynamic model. The xy phase diagrams on the next page (figures 1 and 2) illustrate the homogeneous behaviour when no parameters are available and the heterogeneous azeotropic behaviour when properly fitted parameters are used. The majority of the default interaction parameters for activity coefficient models in HYSYS have been regressed based on VLE data from DECHEMA, Chemistry Data Services.

Fig. 1 - Interaction Parameters set to 0.

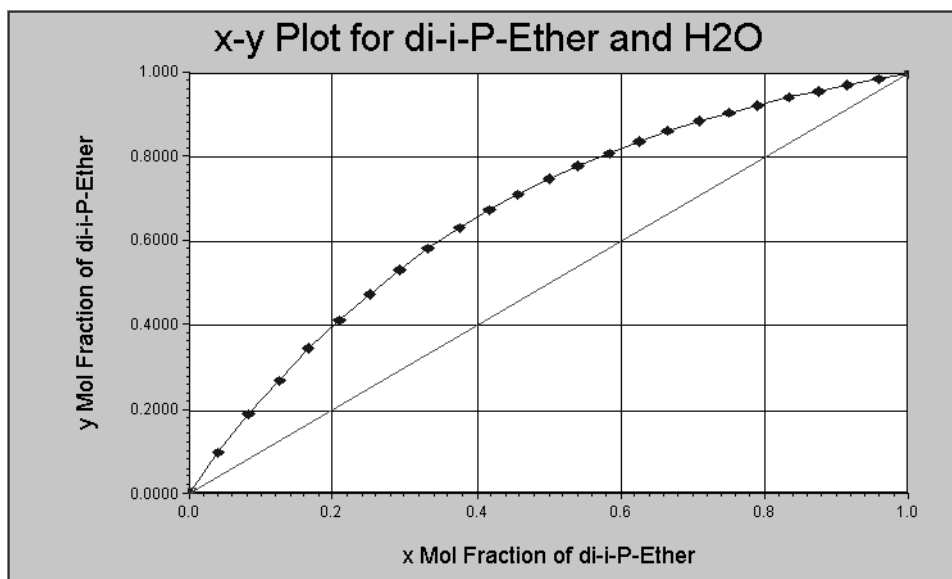
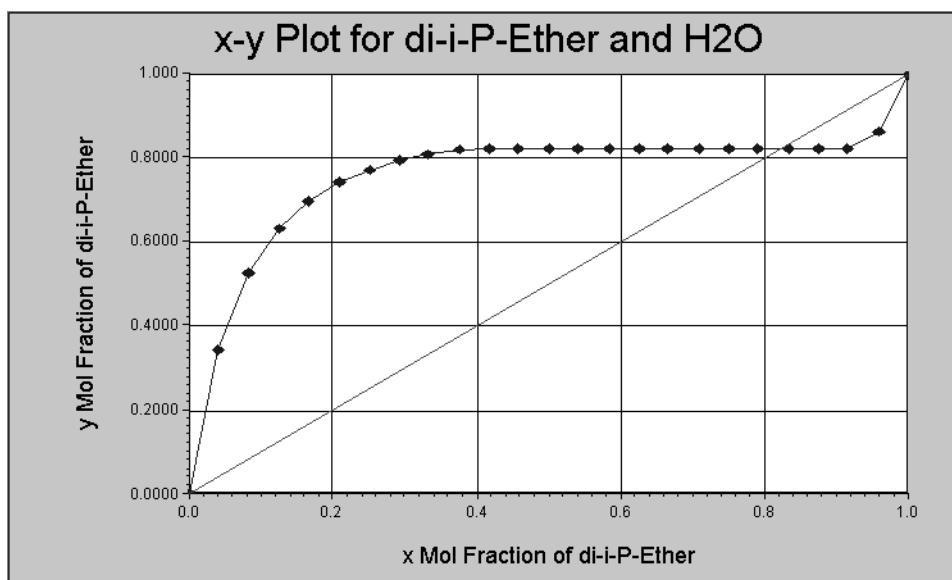


Fig. 2 - Using the Default HYSYS Interaction Parameters.



Exercise 2

Phenol/H2O Binary

This binary shows the importance of ensuring that properly fitted interaction parameters for the conditions of your simulation are used. The default parameters for the Phenol/H2O system have been regressed from the DECHEMA Chemistry data series and provide very accurate vapour-liquid equilibrium since the original data source ⁽¹⁾ was in this format. However, the Phenol/Water system is also shown to exhibit liquid-liquid behaviour ⁽²⁾. A set of interaction parameters can be obtained from sources such as DECHEMA and entered into HYSYS. The following example illustrates the poor LLE prediction than can be produced by comparing the results using default interaction parameters and specially regressed LLE parameters.

1. Open the case **Phenolh2o.hsc**.
2. Enter the following conditions for stream **Phenol/H2O**:

Conditions	
Temperature	40°C
Pressure	1 atm
Molar Flow	1 kgmole/h (1 lbmole/hr)
Composition	
Phenol	25 mole %
H2O	75 mole %



What phase(s) are present? _____

To provide a better prediction for LLE at 40 °C (105 °F) the following A_{ij} interaction parameters are to be entered. To enter the parameters do the following:

1. Close the stream view and press the **Enter Basis Environment** button.
2. Ensure the Fluid Package view is open and select the **Binary Coeffs** tab.
3. Enter the A_{ij} interaction parameters as shown here:

	Phenol	H2O
Phenol	...	3891.142
H2O	-1248.516	...

4. Select the α_{ij}/C_{ij} radio button.
5. Enter an $\alpha_{ij} = 0.2$.
6. Close the Fluid Package view.
7. Return to the simulation environment by pressing the **Return to Simulation Environment** button.
8. Open the stream view for **Phenol/H2O**.



What phase(s) are present now? _____

What are the compositions? _____

The figures on the following page (figures 3 and 4) show the difference between the two sets of interaction parameters. Therefore, care must be exercised when simulating LLE as almost all the default interaction parameters for the activity coefficient models in HYSYS are for VLE.

Fig. 3 - Using the Default (VLE) Interaction Parameters.

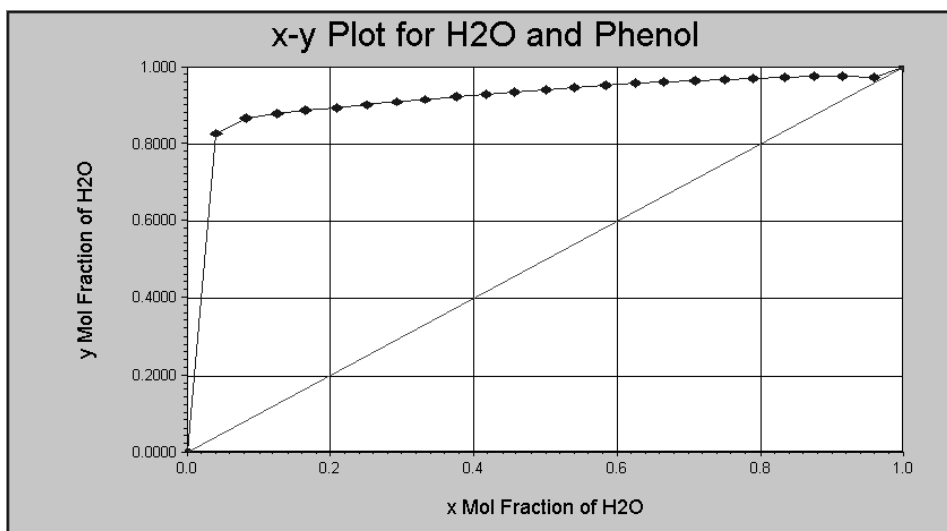
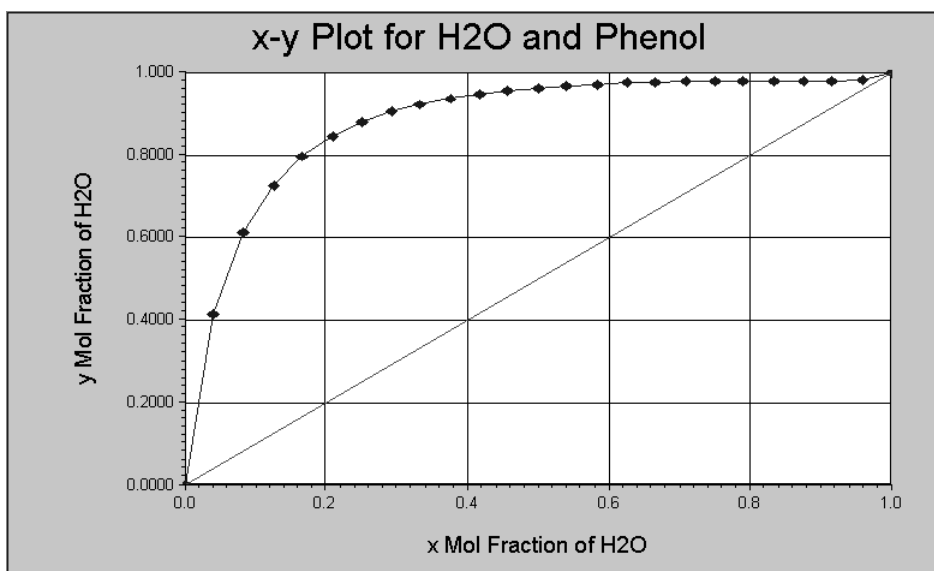


Fig. 4 - Using the Fitted (LLE Optimized) Interaction Parameters.



Exercise 3

Benzene/Cyclohexane/H₂O Ternary

This example again illustrates the importance of having interaction parameters and also discusses how the user can obtain parameters from regression. To illustrate the principles do the following:

1. Open the case **Ternary.hsc**.
2. Enter the following stream conditions for **Benzene/CC6/H₂O**:

Conditions	
Temperature	25°C
Pressure	1 atm
Composition	
Benzene	20 mole %
H ₂ O	20 mole %
CC6	60 mole %



How many phases are present? _____

To provide a more precise simulation the missing CC6/H₂O interaction parameter has to be obtained. Fortunately, some data is available at 25°C giving the liquid-liquid equilibrium between CC6 and H₂O. Using this data, and the regression capabilities within **DISTIL**, an AEA Technology Engineering Software conceptual design and thermodynamic regression product, you can obtain new interaction parameters. The temperature dependent B_{ij} parameters are to be left at 0 and the α_{ij} term is to be set to **0.2** for the **CC6/H₂O**. To implement these parameters, proceed with the steps on the following page.

1. Return to the Basis Environment by pressing the *Enter Basis Environment* button.
2. Open the Fluid Package view and move to the **Binary Coeffs** tab.
3. Enter the data in the A_{ij} matrix as shown here:

	Benzene	H2O	Cyclohexane
Benzene	---	3719.395	286.977
H2O	4843.376	---	3589.973
Cyclohexane	-33.395	5645.254	---

4. Select the α_{ij}/C_{ij} radio button.
5. Enter a CC6/H2O α_{ij} value of **0.2**.
6. Close the Fluid Package view.
7. Return to the Simulation Environment.
8. Open the stream **Benzene/CC6/H2O**.



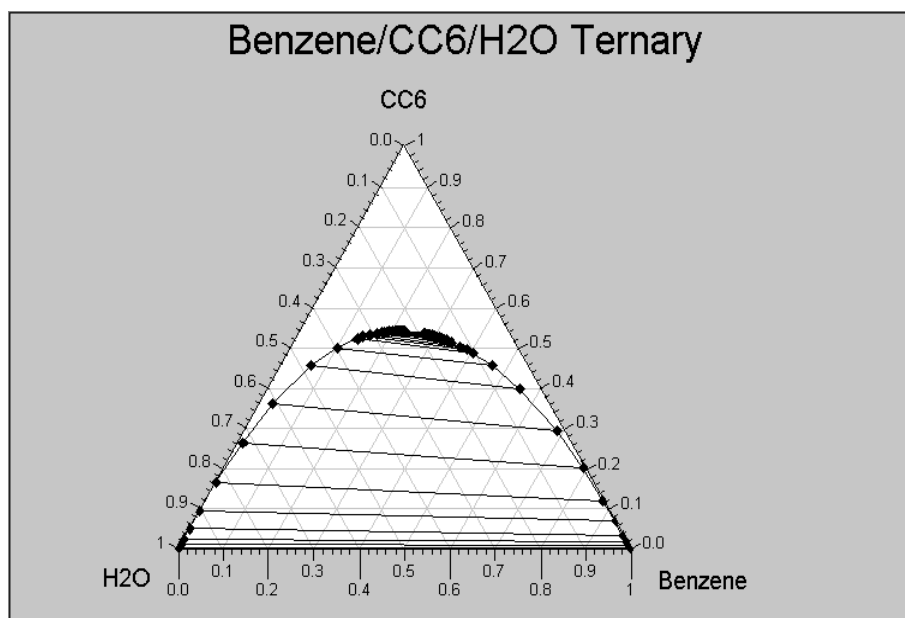
How many phases are now present? _____

What are the compositions? _____

The figures on the following page (figures 5 and 6) clearly show the behaviour of the ternary system. Without the regressed CC6/H2O binary, the thermodynamic property package incorrectly predicts the system to be miscible at higher CC6 concentrations. This prediction is correct given properly regressed CC6/H2O parameters.

References

1. Schreinemakers F.A.H., *Z. Phys. Chem.* 35, 459 (1900).
2. Hill A.E. and Malisoff W.M., *J. Am. Chem. Soc.* 48 (1926) 918.

Fig. 5 - Without Regressed CC6/H₂O Interaction Parameters.Fig. 6 - With Regressed CC6/H₂O Interaction Parameters.